Notes:
1. Untranslatable words are replaced with asterisks (****).
2. Texts in the figures are not translated and shown as it is.

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FULL CONTENTS

[Claim(s)]
[Claim 1] The production method of the metal oxide precursor sol characterized by adding the water to said metal alkoxide at the temperature not more than -20 degree C in the method of hydrolyzing and polymerizing one sort or two sorts or more of metal alkoxide, and manufacturing metal oxide precursor sol.
[Claim 2] The production method of metal oxide precursor sol according to claim 1 with which metal oxide precursor sol is manufactured without using a polydent compound.
[Claim 3] Metal alkoxide The alkali metal from the 2nd period of the periodic table to the 6th period, the [an alkaline earth metal element and] -- the [from the 3rd period of 3B group element and the periodic table to the 6th period] -- the [4B group element and] -- 5B group element -- The element chosen from the group which consists of a transition metal element and lanthanoids, The combination of one sort of metal alkoxide, and two or more sorts of metal alkoxide, the compound alkoxide obtained by the reaction between two or more sorts of metal alkoxide, Or the production method of metal oxide precursor sol according to claim 1 or 2 which is compound alkoxide obtained by a reaction with one sort or two sorts or more of metal alkoxide, one sort, or two sorts or more of metal salts.
[Claim 4] The production method of metal oxide precursor sol according to claim 1 to 3 whose metal oxide is In2O3, SnO2, or In2O3-SnO2.
[Claim 5] The production method of metal oxide precursor sol according to claim 1 to 3 which is the multiple oxide with which a metal oxide has perovskite type structure.
[Claim 6] The production method of the metal oxide precursor sol according to claim 1 to 5 which adds the water to metal alkoxide in [temperature] -50 degree-C--80 degree C.
[Claim 7] The production method of the metal oxide Plastic solid characterized by using the metal oxide precursor sol obtained by the production method according to claim 1 to 6.
[Claim 8] The production method of the metal oxide Plastic solid according to claim 7 which is made to crystallize the metal oxide gel which forms the pellicle, and forms the pellicle of a metal oxide in the coated material surface after applying metal oxide precursor sol on the surface of a coated material and forming the pellicle of a metal oxide gel in the coated material surface.
[Claim 9] Remove under a reduced pressure of the solvent of metal oxide precursor sol, and hyperviscous sol is prepared. The production method of the metal oxide Plastic solid according to claim 7 which is made to crystallize the metal oxide gel which forms the fiber, and forms the fiber of a metal oxide after carrying out spinning of the sol and forming the fiber of a metal oxide gel.

[Detailed Description of the Invention]
[0001]
[Field of the Invention] In order that this invention may form the pellicle of functional metal oxides, such as transparent conductive pellicle, such as pellicle [of a metal oxide], for example, In2O3-, SnO2 (ITO), and dielectric membrane of Pb(Zr, Ti) O3 grade, etc. in the surfaces, such as glass, Ceramics Sub-Division, and plastics It is related with the method of manufacturing the metal oxide precursor sol used, and the method of manufacturing metal oxide Plastic solids, such as pellicle of a metal oxide, using the metal oxide precursor sol.
[0002]
[Description of the Prior Art] For forming the pellicle of a metal oxide on the surface of a substrate using a sol-gel method, After using metal alkoxide as a raw material, hydrolyzing and polymerizing it, preparing substrate oxide precursor sol, applying the obtained sol on the surface of a substrate and forming the pellicle of a metal oxide gel in the substrate surface, the gel film is heat-treated at a suitable temperature. However, it is difficult to prepare homogeneous sol for which homogeneous membrane formation is possible by metal alkoxide except silicon alkoxide, generally, since the hydrolysis velocity is very quick. Then, some methods for controlling the hydrolysis velocity of metal alkoxide are examined.
[0003] If there is the method of making it extremely low and concentration of metal alkoxide is carried out in this way as the inhibition method of the hydrolysis velocity of metal alkoxide, for example, homogeneous membrane formation of sol is possible. However, since the thickness of the film obtained at 1 time of a membrane formation process becomes very thin, this method is not an effective method from an industrial standpoint. Moreover, the concentration of metal alkoxide is increased, and the organic compound in which a polydent is possible is added as a method of controlling hydrolysis velocity and obtaining the sol which can form membranes, and some methods of stabilizing metal alkoxide are proposed. By formation of the alumina membrane which used for example, aluminium s-butoxide as the starting material [formation of the titania pellicle with which beta-diketone is effective (the Ceramic Society of Japan treatise magazine, 97, 396 (1989)) and with which it used titanium isopropoxide as the starting material] The thing (the Ceramic Society of Japan treatise magazine, 97, 213 (1989)) with effective beta-diketone is reported, respectively effectively [1,3-butanediol] (Hisao Koshiba, the Toyohashi University of Technology doctoral dissertation, Heisei 5(1993) March). Moreover, it is reported by formation of the zirconia pellicle which used zirconium n-butoxide as the starting material that use of diethylene glycol is effective (a ceramic industry association magazine, 95, 942 (1987)). Furthermore, the report that use of beta-diketone or alkanolamine is effective also in synthesis of multiple oxides, such as PbTiO3 and Pb(Zr, Ti) O3, is journal OBU American ceramic SOSAIATI (Journal). of American Ceramics It is indicated by Society, 74, 1407 (1991) and the Ceramic Society of Japan treatise magazine, and 98 and 745 (1990).
[0004] Moreover, a physics OBU Ching film (Physics of TinFilm), The report about the production method of the oxide film using a hydrolysis and aqua-complex of various mineral salt, such as a chloride, sulfate, nitrate, and ammonium salt, is made by 5, p87 (1969), and Academic Press (Academic Press). Furthermore, using nitric acid indium and chlorination tin instead of metal alkoxide for preparation of sol of In2O3-SnO2 as a multiple oxide is shown in the Ceramic Society of Japan treatise

magazine, and 102 and 200 (1994).
[0005]
[Problem(s) to be Solved by the Invention] However, [as described above, according to the method of making stabilize metal alkoxide by addition of a polydent compound, and controlling the hydrolysis velocity of metal alkoxide, can prepare homogeneous sol for membrane formation easily, but] Many organic substances which are hard to disassemble in a high boiling point into sol or a gel film will live together. As a result, it is necessary to heat-treat a gel film at about 500-degree C high temperature for removal of that organic substance. Moreover, since many organic substances remain in a gel film, if a gel film is heat-treated, membranous weight loss will become large. In other words, many pores are generated by removal of the organic substance from a gel film in a film, and it becomes the cause of the defect of the obtained metal oxide thin film. On the other hand, in order to remove the pore in a film, energy excessive for eburnation of the pellicle is needed.
[0006] Moreover, as described above, the method of using a metal salt is a pyrolysis method fundamentally, and many problems will be produced in the membraneous quality after heat-treatment.
[0007] This invention is made in view of the above situations, and homogeneous metal oxide precursor sol for which homogeneous membrane formation is possible can be prepared. When [and] the quantity of the organic substance which remains in sol or the gel film after membrane formation forms membranes, using offering the method that little metal oxide precursor sol can be manufactured, and metal oxide precursor sol There is no necessity of there being little quantity of the organic substance which remains on a gel film, and heat-treating the gel film in high temperature for organic substance removal for this reason. Treatment at low temperature is comparatively possible, a homogeneous metal oxide thin film without air bubbles can be formed, and it aims at offering the method that the metal oxide Plastic solid which does not need energy excessive for eburnation of pellicle can be manufactured.
[0008]
[Means for Solving the Problem] Invention concerning Claim 1 is characterized by adding the water to said metal alkoxide at the temperature not more than -20 degree C in the method of hydrolyzing and polymerizing one sort or two sorts or more of metal alkoxide, and manufacturing metal oxide precursor sol.
[0009] Invention concerning Claim 2 is characterized by manufacturing metal oxide precursor sol without using a polydent compound in a production method according to claim 1.
[0010] Since the hydrolysis velocity of metal alkoxide is controlled by performing addition of the water to metal alkoxide at the low temperature of less than -20 degree C according to the production method of invention concerning Claim 1, homogeneous metal oxide precursor sol in which homogeneous membrane formation is possible can be prepared. And like the production method of invention concerning Claim 2, since it is not necessary to use a polydent compound, when membranes are formed using the obtained metal oxide precursor sol, there is little quantity of the organic substance which remains in a gel film.
[0011] Invention concerning Claim 3 is set to a production method according to claim 1 or 2. As metal alkoxide, the alkali metal from the 2nd period of the periodic table to the 6th period, the [an alkaline earth metal element and] -- the [from the 3rd period of 3B group element and the periodic table to the 6th period] -- the [4B group element and] -- 5B group element -- The element chosen from the group which consists of a transition metal element and lanthanoids, The combination of one sort of metal alkoxide, and two or more sorts of metal alkoxide, the compound alkoxide obtained by the reaction

between two or more sorts of metal alkoxide, Or it is characterized by using the compound alkoxide obtained by a reaction with one sort or two sorts or more of metal alkoxide, one sort, or two sorts or more of metal salts.

[0012] Invention concerning Claim 4 is characterized by a metal oxide being In2O3, SnO2, or In2O3-SnO2 in a production method according to claim 1 to 3.

[0013] Invention concerning Claim 5 is characterized by a metal oxide being a multiple oxide which has perovskite type structure in a production method according to claim 1 to 3.

[0014] Invention concerning Claim 6 is characterized by adding the water to metal alkoxide in [temperature] -50 degree-C--80 degree C in a production method according to claim 1 to 5.

[0015] Invention concerning Claim 7 is characterized by manufacturing a metal oxide Plastic solid using the metal oxide precursor sol obtained by the production method according to claim 1 to 6.

[0016] Invention concerning Claim 8 applies metal oxide precursor sol on the surface of a coated material in a production method according to claim 7. After forming the pellicle of a metal oxide gel in the coated material surface, the metal oxide gel which forms the pellicle is crystallized, and it is characterized by forming the pellicle of a metal oxide in the coated material surface.

[0017] [according to the production method of invention concerning Claim 7 / the homogeneous metal oxide precursor sol obtained by the production method of invention concerning Claim 1] like the production method of invention which relates, for example to Claim 8 Since it applies on the surface of a coated material and the pellicle of a metal oxide gel is formed, there are few amounts of residual organic substances in the gel film. For this reason, the pellicle of a homogeneous metal oxide without air bubbles is obtained by not heat-treating the gel film in high temperature for organic substance removal, and crystallizing a metal oxide gel.

[0018] Invention concerning Claim 9 removes the solvent of metal oxide precursor sol under a reduced pressure in a production method according to claim 7. After preparing hyperviscous sol, carrying out spinning of the sol and forming the fiber of a metal oxide gel, the metal oxide gel which forms the fiber is crystallized, and it is characterized by forming the fiber of a metal oxide.

[0019]

[Embodiment of the Invention] An embodiment is explained suitably [this invention] hereafter. In the production method of metal oxide precursor sol concerning this invention, one sort or two sorts or more of metal alkoxide is used as a starting material, water is added at the temperature not more than -20 degree C to that metal alkoxide, and metal alkoxide is hydrolyzed and polymerized.

[0020] Although it is dependent on the stability of metal alkoxide and the addition temperature of the water to metal alkoxide should just be -20 degrees C or less in temperature, it is more desirable to add the water to metal alkoxide in [temperature] -50 degree-C--80 degree C depending on the kind of metal alkoxide. - even if it adds a polydent compound to metal alkoxide and does not make it not stabilize metal alkoxide by adding water at the low temperature of 20 degrees C or less Metal alkoxide becomes possible [performing hydrolysis / polymerization reaction by high concentration], and the high-concentration metal oxide precursor sol which does not contain unnecessary organic substances, such as a polydent compound, can be obtained. As a result, when that metal oxide precursor sol was used, a gel film with little organic substance content, a gel fiber, a bulk gel, etc. are obtained and an organic substance is desorbed from those gels by heat-treatment etc., the destruction of a detailed organization and the amount of remains pores in the acquired Plastic solid can be reduced.

[0021] As usable metal alkoxide, the alkali metal from the 2nd period of the periodic table to the 6th

period, the [an alkaline earth metal element and] -- the [from the 3rd period of 3B group element and the periodic table to the 6th period] -- the [4B group element and] -- 5B group element -- It is not limited in particular that what is necessary is just the combination of one sort of metal alkoxide of the element chosen from the group which consists of a transition metal element and lanthanoids, or two or more sorts of metal alkoxide. Moreover, you may be compound alkoxide obtained by a reaction with the compound alkoxide obtained by the reaction between two or more sorts of metal alkoxide of said element, one sort, or two sorts or more of metal alkoxide, one sort, or two sorts or more of metal salts. Furthermore, it is also possible to use it combining these.

[0022] As compound alkoxide obtained by the reaction between two or more sorts of metal alkoxide the [the compound alkoxide obtained by the reaction of alkoxide of an alkali metal or an alkaline earth metal, and alkoxide of a transition metal, and] -- compound alkoxide as a complex salt obtained with the combination of 3B group element is used. for example, -- BaTi -- (-- OR --) -- six -- SrTi -- (-- OR --) -- six -- BaZr -- (-- OR --) -- six -- SrZr -- (-- OR --) -- six -- LiNb -- (-- OR --) -- six -- LiTa -- (-- OR --) -- six -- and -- these -- combination -- LiVO -- (-- OR --) -- four -- MgAl -- two -- (-- OR --) -- eight -- etc. -- it is . moreover, (RO) 3SiOAl (OR') A reactant and its condensation polymer with silicon alkoxide, such as 2, (RO)3SiOTi(OR')3, (RO)3SiOZr(OR')3, (RO)3SiOB(OR')2, (RO)3SiONb(OR')4, and (RO)3SiOTa(OR')4, are also used. Here, R and R' shows an alkyl group. Moreover, as compound alkoxide obtained by a reaction with one sort or two sorts or more of metal alkoxide, one sort, or two sorts or more of metal salts, the compound obtained by the reaction of metal salts, such as a chloride, nitrate, sulfate, acetate, formate, and oxalate, and alkoxide is used.

[0023] The transparent conductive material of as [whose metal oxide which it is finally going to obtain especially is In2O3, SnO2, or In2O3-SnO2 (ITO)], When it is dielectric material, such as a multiple oxide which has perovskite type structure, and manufactures those precursor sol, the production method concerning this invention is effective.

[0024] Although the carbon number in particular of the alkoxyl group of metal alkoxide is not limited, from content oxide concentration, the ease [an organic substance] of desorption, the ease of acquisition, etc., carbon numbers 1-4 are more desirable.

[0025] Moreover, if the water used for a metal alkoxide raw material and a hydrolysis does not solidify as a solvent used at the temperature which is meltable respectively and adds water, a single solvent or a partially aromatic solvent will be sufficient, and it will not be limited in particular. For example, the combination of polar solvents and a nonpolar solvent is sufficient. From the viscosity in the temperature region which adds water, the ease of removal, etc., especially methanol, ethanol, and propanol that are the alcohol of carbon numbers 1-3 are desirable.

[0026] In order to make it easy to desorb from a solvent after gelling, as for the polydent compound which carries out direct coupling to metal alkoxide, it is desirable to stop the amount used as much as possible. Even if it does not use a polydent compound for a contrary rather according to the method concerning this invention, it is also possible to prepare metal oxide precursor sol. Since the acid amide expressed with RCONR' (R and R' is hydrogen or an alkyl group) which, on the other hand, carries out two or more owners of the functional group in which coordination is possible does not form binding by displacement with an alkoxyl group, it does not solidify at the addition temperature of water, and if removal by volatilization is easy, the use will not interfere.

[0027] Since it changes with the kinds of metallic element and the kinds of alkoxyl group in metal alkoxide, the amount of addition of water cannot be specified. Moreover, since the optimal stable pH

values of sol differ depending on the kind of metallic element, an acid or a base is suitably used together as a catalyst. Although the catalyst in particular to be used is not limited, in order to obtain high grade material, the compound which does not contain a metal component is desirable. For example, as an acid, organic acids, such as mineral acids, such as hydrochloric acid, nitric acid, sulfuric acid, and phosphoric acid, carbonic acid, a way acid, formic acid, acetic acid, and oxalic acid, are used. Moreover, ammonia and amine are used as a base.

[0028] The obtained metal oxide precursor sol can be considered as the gel of various forms, such as bulk, a fiber, and pellicle, by the difference in the shaping method. When forming the pellicle of a metal oxide gel and forming the pellicle of a functional metal oxide especially, the production method concerning this invention is effective.

[0029] Especially the shaping method of a gel should just be a method which it is not limited but can generally be enforced as the shaping method using sol liquid. For example, after adding the water of a quantity required for gelling to metal alkoxide, the cast of the bulk object is carried out into a container, and it is acquired by neglecting it at the temperature below a room temperature or the boiling point of the used solvent. Moreover, a fiber object is acquired by carrying out **** (spinning) of the hyperviscous sol, after adding water to metal alkoxide, removing a solvent partially and adjusting viscosity. Pellicle is obtained by applying sol liquid on a base forming. As the method of spreading, a dip coat, a spin coat, a flow coat, etc. can use the method currently generally enforced.

[0030] The Plastic solid of the metal oxide gel obtained from metal oxide precursor sol turns into a functional oxide Plastic solid by performing treatment according to the purposes, such as an optical exposure of heat-treatment, ultraviolet radiation, etc.

[0031] In the method of using metal alkoxide as a starting material and manufacturing a metal oxide Plastic solid using a sol-gel method, the stability of precursor sol and moldability, such as membrane formation nature, are very important. Generally, in order to raise the stability of sol, the degree of polymerization of metal alkoxide is enlarged (in the stage of solation). the inorganic polymer which has not a meeting of a metal alkoxide molecule but M-O-M (metal-oxygen-metal) binding is generated -- **** -- the method of adding a polydent compound is effective. However, since the stability over the water of metal alkoxide except silicon alkoxide was very low, it was very difficult for it to obtain homogeneous sol by the conventional method. On the other hand, if a polydent compound is added, it is possible to obtain stable sol easily, but many remains organic substances will be included in sol and a gel, and it is necessary to remove a remains organic substance out of a gel in process of final mineralization. In order for a detailed organization to get worse and to improve the detailed organization by the destruction of an organization and the generation of a pore in a Plastic solid with removal of the remains organic substance, heat-treatment etc. will take the energy more than needed. On the other hand, according to the method concerning this above-mentioned invention, without adding an excessive polydent compound, hydrolysis / polymerization reaction of metal alkoxide after addition of water can be inhibited, and it becomes possible to obtain stable high-concentration metal oxide precursor sol. And there is little quantity of the remains organic substance in the obtained gel, and it can obtain target high-performance material by after-treatment of low energy.

[0032]

[Example] Next, the more concrete work example of this invention is explained.

[Preparation of metal oxide precursor sol]

<Work examples 1-14> Indium alkoxide was added to ethanol so that the solid content concentration of

In2O3 might become 15 weight %. Moreover, distilled water-ethanol mixed liquor was prepared so that the solid content concentration of In2O3 might become 10 weight %, when it added in an indium alkoxide solution. After cooling an indium alkoxide solution and distilled water-ethanol mixed liquor to a predetermined temperature in a refrigerant, both liquid was mixed and liquid was returned to the room temperature after that. This obtained homogeneous In2O3 precursor sol. The comparative examples 1-3 later mentioned to Table 1 also combine the blending ratio of coal and synthetic conditions, and it collects, and is shown. Among Table 1, the molar ratio of H2 O/In is shown in the column of the "amount of addition" of "water", and hydrochloric acid (HCl) adjusted "pH" of "water" in it. Moreover, "O" of the column of "the state of sol" in Table 1 shows that transparent homogeneous sol was prepared.

[0033]

[Table 1]

	原料	溶媒	水		添加温度（℃）	ゾルの状態
			添加量	pH		
実施例 1	In(OCH3)3	エタノール	0.6	1	-75	○
2	In(OC2H5)3	エタノール	0.6	1	-75	○
3	In(O-n-C3H7)3	エタノール	0.6	1	-75	○
4	In(O-i-C3H7)3	エタノール	0.6	1	-75	○
5	In(O-n-C4H9)3	エタノール	0.6	1	-75	○
6	In(O-s-C4H9)3	エタノール	0.6	1	-75	○
7	In(O-t-C4H9)3	エタノール	0.6	1	-75	○
8	In(O-s-C4H9)3	メタノール	0.6	1	-75	○
9	In(O-s-C4H9)3	1-プロパノール	0.6	1	-75	○
10	In(O-s-C4H9)3	2-プロパノール	0.6	1	-75	○
11	In(O-s-C4H9)3	エタノール	0.8	1	-75	○
12	In(O-s-C4H9)3	エタノール	0.6	3	-75	○
13	In(O-s-C4H9)3	エタノール	0.6	5	-75	○
14	In(O-s-C4H9)3	ジメチルホルムアミド	0.6	1	-50	○
比較例 1	In(O-s-C4H9)3	エタノール	0.6	1	室温	部分的ゲル化
2	In(O-s-C4H9)3	2-ブタノール	0.6	1	室温	部分的ゲル化
3	In(O-s-C4H9)3	2-ブタノール-アセチルアセトン	1	1	室温	○

[0034] <Comparative example 1> Tree s-butoxy indium was added to ethanol so that the solid content concentration of In2O3 might become 5 weight %. Moreover, 1N hydrochloric acid-ethanol mixed liquor (the molar ratio of H2 O/In is 0.6) was prepared so that the solid content concentration of In2O3 might become 2.5 weight %, when it added in a tree s-butoxy indium solution. 1N hydrochloric acid-ethanol mixed liquor was added in the indium alkoxide solution at the room temperature.

[0035] <Comparative example 2> Tree t-butoxy indium was added to 2-butanol so that the solid content concentration of In2O3 might become 5 weight %. Moreover, 1N hydrochloric acid-2-butanol mixed liquor (the molar ratio of H2 O/In is 0.6) was prepared so that the solid content concentration of In2O3

might become 2.5 weight %, when it added in a tree t-butoxy indium solution. 1N hydrochloric acid-2-butanol mixed liquor was added in the indium alkoxide solution at the room temperature.

[0036] In a comparative example 1 and a comparative example 2, it was not able to become cloudy and gel locally from the part where water was added, respectively, and homogeneous sol was not able to be obtained.

[0037] <Comparative example 3> Tree t-butoxy indium was added to 2-butanol, further, acetylacetone was added so that it might become indium and equimolar, and the indium alkoxide solution with which the solid content concentration of In2O3 becomes 5 weight % was prepared. Moreover, 1N hydrochloric acid-2-butanol mixed liquor (the molar ratio of H2 O/In is 1) was prepared so that the solid content concentration of In2O3 might become 2.5 weight %, when it added in an indium alkoxide solution. 1N hydrochloric acid-2-butanol mixed liquor was added in the indium alkoxide solution at the room temperature. When the solid content concentration of In2O3 was to 2.5 weight %, the homogeneous solution was obtained, but at 3 weight % or more, it became cloudy partially.

[0038] <Work example 15> Tetra s-butoxy tin was added to ethanol so that the solid content concentration of a stannic acid ghost might become 20 weight %. Moreover, 1N hydrochloric acid-ethanol mixed liquor was prepared so that the solid content concentration of SnO2 might become 10 weight %, when it added in a tetra-s-butoxy tin solution. After cooling a tin alkoxide solution and 1N hydrochloric acid-ethanol mixed liquor to -25 degree C in a refrigerant, both liquid was mixed and liquid was returned to the room temperature after that. This obtained homogeneous SnO2 precursor sol.

[0038] <Comparative example 4> Tetra s-butoxy tin was added to ethanol and 1N hydrochloric acid-ethanol mixed liquor was added at the room temperature in the tin alkoxide solution. As a result, solid content concentration of SnO2 was not able to obtain homogeneous SnO2 precursor sol at 2.5 weight % or more.

[0039] <Work examples 16-32> Indium alkoxide and tin alkoxide were added to ethanol so that the solid content concentration of a metal oxide might become 15 weight %, and the mixed solution of metal alkoxide was prepared. Moreover, distilled water-ethanol mixed liquor was prepared so that the solid content concentration of a metal oxide might become 10 weight %, when it added to the mixed solution of metal alkoxide. After cooling the mixed solution of metal alkoxide, and distilled water-ethanol mixed liquor to a predetermined temperature in a refrigerant, both liquid was mixed and liquid was returned to the room temperature after that. This obtained homogeneous In2O3-SnO2 (ITO) precursor sol. The blending ratio of coal and synthetic conditions are collectively shown in Table 2. Among Table 2, the molar ratio of H2O/(In+Sn) is shown in the column of the "amount of addition" of "water", and hydrochloric acid (HCl) adjusted "pH" of "water" in it. Moreover, "O" of the column of "the state of sol" in Table 1 shows that transparent homogeneous sol was prepared.

[0040]

[Table 2]

度 (℃)	-75	-75	-75	-75	-75	-75	-75	-75	-75	-75	-75	-75	-75	-50	-75	-75	-75
ゾルの状態	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○

		原料				水		添加温度（
		Inｱﾙｺｷｼﾄﾞ	Snｱﾙｺｷｼﾄﾞ	SnO2重量%	溶媒	添加量	pH	
実施例	16	In(O-s-C4H9)3	Sn(OCH3)4	10	ｴﾀﾉｰﾙ	0.6	1	-75
	17	In(O-s-C4H9)3	Sn(OC2H5)4	10	ｴﾀﾉｰﾙ	0.6	1	-75
	18	In(O-s-C4H9)3	Sn(O-n-C3H7)4	10	ｴﾀﾉｰﾙ	0.6	1	-75
	19	In(O-s-C4H9)3	Sn(O-i-C3H7)4	10	ｴﾀﾉｰﾙ	0.6	1	-75
	20	In(O-s-C4H9)3	Sn(O-n-C4H9)4	10	ｴﾀﾉｰﾙ	0.6	1	-75
	21	In(O-s-C4H9)3	Sn(O-s-C4H9)4	10	ｴﾀﾉｰﾙ	0.6	1	-75
	22	In(O-s-C4H9)3	Sn(O-t-C4H9)4	10	ｴﾀﾉｰﾙ	0.6	1	-75
	23	In(O-s-C4H9)3	Sn(O-s-C4H9)4	2	ｴﾀﾉｰﾙ	0.6	1	-75
	24	In(O-s-C4H9)3	Sn(O-s-C4H9)4	5	ｴﾀﾉｰﾙ	0.6	1	-75
	25	In(O-s-C4H9)3	Sn(O-s-C4H9)4	15	ｴﾀﾉｰﾙ	0.6	1	-75
	26	In(O-s-C4H9)3	Sn(O-s-C4H9)4	20	ｴﾀﾉｰﾙ	0.6	1	-75
	27	In(O-s-C4H9)3	Sn(O-s-C4H9)4	10	ｴﾀﾉｰﾙ	0.6	3	-75
	28	In(O-s-C4H9)3	Sn(O-s-C4H9)4	10	ｴﾀﾉｰﾙ	0.6	5	-75
	29	In(O-s-C4H9)3	Sn(O-s-C4H9)4	10	ｼﾞﾒﾁﾙﾎﾙﾑｱﾐﾄﾞ	0.6	1	-50
	30	In(O-s-C4H9)3	Sn(O-s-C4H9)4	10	ｴﾀﾉｰﾙ	0.8	1	-75
	31	In(O-i-C3H7)3	Sn(O-s-C4H9)4	10	ｴﾀﾉｰﾙ	0.8	1	-75
	32	In(O-i-C3H7)3	Sn(O-i-C3H7)4	10	ｴﾀﾉｰﾙ	0.6	1	-75

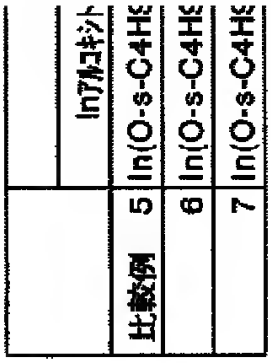
[0041] <Comparative example 5> Tree t-butoxy indium and tetra-s-butoxy tin were added to 2-butanol so that the solid content concentration of a metal oxide might become 5 weight %, and the mixed solution of metal alkoxide was prepared. Moreover, 1N hydrochloric acid-2-butanol mixed liquor (the molar ratio of H2 O/In is 0.6) was prepared, and the mixed liquor was added to the mixed solution of metal alkoxide so that the solid content concentration of a metal oxide might become 2.5 weight %, when it added to the mixed solution of metal alkoxide. It was not able to become cloudy and gel locally

from the part where water (1N hydrochloric acid-2-butanol mixed liquor) was added, and homogeneous sol was not able to be obtained. In addition, the comparative examples 6 and 7 later mentioned to Table 3 also combine the blending ratio of coal and the synthetic conditions at this time, and it collects, and is shown. Among Table 3, the molar ratio of H2 O/In is shown in the column of the "amount of addition" of "water", and hydrochloric acid (HCl) adjusted "pH" of "water" in it. Moreover, "O" of the column of "the state of sol" in Table 3 shows that transparent homogeneous sol was prepared.

[0042]

[Table 3]

原料			溶媒	水		添加温度（℃）	ゾルの状態
ｷｼﾄﾞ	Snｱﾙｺｷｼﾄﾞ	SnO2重量%		添加量	pH		
C4H9)3	Sn(O-s-C4H9)4	10	2-ﾌﾞﾀﾉｰﾙ	0.6	1	室温	部分的ｹﾞﾙ化
C4H9)3	Sn(O-s-C4H9)4	10	ｼﾞﾒﾁﾙﾎﾙﾑｱﾐﾄﾞ	0.6	1	室温	部分的ｹﾞﾙ化
C4H9)3	Sn(O-s-C4H9)4	10	2-ﾌﾞﾀﾉｰﾙ	0.6	1	室温	○



[0043] <Comparative example 6> Tree t-butoxy indium and tetra-s-butoxy tin were added to N, N dimethylformamide (DMF) so that the solid content concentration of a metal oxide might become 5 weight %, and the mixed solution of metal alkoxide was prepared. Moreover, 1N hydrochloric acid-DMF mixed liquor (the molar ratio of H2O/(In+Sn) is 0.6) was prepared, and the mixed liquor was added to the mixed solution of metal alkoxide so that the solid content concentration of a metal oxide might become 2.5 weight %, when it added to the mixed solution of metal alkoxide. It was not able to become cloudy and gel locally like the comparative example 5 from the part where water was added, and homogeneous sol was not able to be obtained.

[0044] <Comparative example 7> Tree t-butoxy indium and tetra-s-butoxy tin were added to 2-butanol so that the solid content concentration of a metal oxide might become 5 weight %, and the mixed solution of metal alkoxide was prepared. Moreover, 1N hydrochloric acid-2-butanol mixed liquor (the molar ratio of H2O/(In+Sn) is 1) was prepared so that the solid content concentration of a metal oxide might become 2.5 weight %, when it added to the mixed solution of metal alkoxide. After adding indium alkoxide and tin alkoxide, and acetylacetone of equimolar to a mixed solution, 1N hydrochloric acid-2-butanol mixed liquor was added to the mixed solution of metal alkoxide at the room temperature. When the solid content concentration of a metal oxide was to 2.5 weight %, the homogeneous solution was obtained, but at 3 weight % or more, it became cloudy partially.

[0045] <Work examples 33-43> Only titanium and equimolar added metal barium in the ethanol solution of titanium alkoxide, and the solid content concentration of the metal oxide obtained the ethanol solution of Ba-Ti compound alkoxide which is 20 weight %. Moreover, distilled water-ethanol mixed liquor was prepared so that the solid content concentration of a metal oxide might become 1.0 weight %, when it added in a compound alkoxide solution. After cooling a Ba-Ti compound alkoxide solution and distilled water-ethanol mixed liquor to a predetermined temperature in a refrigerant, both liquid was mixed and liquid was returned to the room temperature after that. This obtained homogeneous BaTiO3 precursor sol. The comparative examples 8-9 later mentioned to Table 4 also combine the blending ratio of coal and synthetic conditions, and it collects, and is shown. Among Table 4, the molar ratio of H2 O/ Ti is shown in the column of the "amount of addition" of "water", and hydrochloric acid (HCl) adjusted "pH" of "water" in it. Moreover, "O" of the column of "the state of sol" in Table 4 shows that transparent homogeneous sol was prepared.

[0046]

[Table 4]

	原料	溶媒	水		添加温度（℃）	ゾルの状態
			添加量	pH		
実施例 33	Ti(OCH3)4	エタノール	1	1	-50	○
34	Ti(OC2H5)4	エタノール	1	1	-50	○
35	Ti(O-n-C3H7)4	エタノール	1	1	-50	○
36	Ti(O-i-C3H7)4	エタノール	1	1	-50	○
37	Ti(O-n-C4H9)4	エタノール	1	1	-50	○
38	Ti(O-s-C4H9)4	エタノール	1	1	-50	○
39	Ti(O-t-C4H9)4	エタノール	1	1	-50	○
40	Ti(OC2H5)4	エタノール	1	3	-50	○
41	Ti(OC2H5)4	エタノール	1	5	-50	○
42	Ti(OC2H5)4	エタノール	1	9	-50	青白色ゾル
43	Ti(OC2H5)4	エタノール	1	1	-25	○
比較例 8	Ti(OC2H5)4	エタノール	1	1	室温	白沈
9	Ti(OC2H4OCH3)4	2-メトキシエタノール	1	1	室温	○
10	Ti(OC2H5)4	エタノール-アセチルアセトン	1	1	室温	○

[0047] O(Zr (Ba, Sr), Ti)3 sol which replaced zirconium alkoxide or metal barium for titanium alkoxide by metal strontium partially was also able to be obtained by the same method as the above.

[0048] <Comparative example 8> Only titanium and equimolar added metal barium in the ethanol solution of tetra-ethoxy titanium, and the ethanol solution of Ba-Ti compound alkoxide was obtained. Although 1N hydrochloric acid (the molar ratio of H2 O/Ti is 1) diluted with ethanol was added in the Ba-Ti compound alkoxide solution, white precipitate was generated for metal oxide concentration as for 0.5 weight %.

[0049] <Comparative example 9> Only titanium and equimolar added metal barium in the 2-methoxyethanol solution of tetramethoxy ethoxy titanium, and the 2-methoxyethanol solution of Ba-Ti compound alkoxide was obtained. Moreover, 1N hydrochloric acid-2-methoxy ethanol mixed liquor (the molar ratio of H2 O/Ti is 1) was prepared, and the mixed liquor was added in the Ba-Ti compound alkoxide solution at the room temperature so that the solid content concentration of BaTiO3 might become 1 weight %, when it added in a compound alkoxide solution. Although sol with solid content concentration of BaTiO3 homogeneous at 1 weight % was obtained, when oxide concentration was made more than 1 weight %, gelling and precipitate were produced partially and homogeneous sol was not able to be obtained.

[0050] <Comparative example 10> Only titanium and equimolar added metal barium in the ethanol solution of tetra-ethoxy titanium, and the ethanol solution of Ba-Ti compound alkoxide was obtained. Moreover, when you add in a compound alkoxide solution, the solid content concentration of BaTiO3 should become 1 weight %, After preparing 1N hydrochloric acid-ethanol mixed liquor (the molar ratio of H2 O/Ti is 1) and adding acetylacetone of the duplex mole of titanium alkoxide in a compound alkoxide solution, 1N hydrochloric acid-ethanol mixed liquor was added. Although homogeneous

BaTiO3 were obtained by this, when oxide concentration was made more than 1 weight %, gelling and precipitate were produced partially and homogeneous sol was not able to be obtained.

[0051] <Work examples 44-53> It is acetic anhydride lead to the ethanol solution of titanium alkoxide and/or zirconium alkoxide. Carried out equimolar addition with the quantity of Ti+Zr, it was made to react at the channeling-back temperature of ethanol for 24 hours, and oxide concentration obtained the ethanol solution of Pb-Zr-Ti compound alkoxide which is 20 weight %. Moreover, distilled water-ethanol mixed liquor was prepared so that the solid content concentration of a metal oxide might become 10 weight %, when it added in a compound alkoxide solution. After cooling a Pb-Zr-Ti compound alkoxide solution and distilled water-ethanol mixed liquor to a predetermined temperature in a refrigerant, both liquid was mixed and it returned to the room temperature. This obtained homogeneous Pb(Zr, Ti) O3 precursor sol. The comparative example 11 mentioned later also combines, summarizes and shows the blending ratio of coal and synthetic conditions in Table 5. Among Table 5, the molar ratio of H2O/(Ti+Zr) is shown in the column of the "amount of addition" of "water", and hydrochloric acid (HCl) or ammonia (NH3) adjusted "pH" of "water" in it. Moreover, "O" of the column of "the state of sol" in Table 1 shows that transparent homogeneous sol was prepared.

[0052]

[Table 5]

	原料			溶媒	水		添加温度（℃）	ゾルの状態
	Tiｱﾙｺｷｼﾄﾞ	Zrｱﾙｺｷｼﾄﾞ	ZrO2ﾓﾙ%		添加量	pH		
実施例 44	Ti(OCH3)4		0	ｴﾀﾉｰﾙ	1	1	-50	○
45	Ti(OC2H5)4		0	ｴﾀﾉｰﾙ	1	1	-50	○
46	Ti(O-i-C3H7)4		0	ｴﾀﾉｰﾙ	1	1	-50	○
47	Ti(OC2H5)4	Zr(OC2H5)4	53	ｴﾀﾉｰﾙ	1	1	-50	○
48		Zr(OC2H5)4	100	ｴﾀﾉｰﾙ	1	1	-50	○
49	Ti(OC2H5)4	Zr(O-n-C4H9)4	53	ｴﾀﾉｰﾙ	1	1	-50	○
50		Zr(O-n-C4H9)4	100	ｴﾀﾉｰﾙ	1	1	-50	○
51	Ti(OC2H5)4	Zr(O-n-C4H9)4	53	ｴﾀﾉｰﾙ	1	3	-50	○
52	Ti(OC2H5)4	Zr(O-n-C4H9)4	53	ｴﾀﾉｰﾙ	1	5	-50	○
53	Ti(OC2H5)4	Zr(O-n-C4H9)4	53	ｴﾀﾉｰﾙ	1	9	-50	青白色ゾル
比較例 11	Ti(OC2H5)4	Zr(O-n-C4H9)4	53	ｴﾀﾉｰﾙ	1	1	室温	白沈

[0053] Even if it transposed titanium alkoxide and/or zirconium alkoxide to partial or the whole quantity, tin alkoxide, or germanium alkoxide, homogeneous sol was able to be obtained by the same method as the above.

[0053] <Comparative example 11> It is acetic anhydride lead to the ethanol solution of tetra-ethoxy titanium and tetra-n-butoxyzirconium (Zr/Ti=53 / 47 molar ratios). Carried out equimolar addition with the quantity of Ti+Zr, it was made to react at the channeling-back temperature of ethanol for 24 hours, and the ethanol solution of Pb-Zr-Ti compound alkoxide which is 10 weight % of oxide concentration was obtained. Although 1N hydrochloric acid (the molar ratio of H2O/(Ti+Zr) is 1) diluted with ethanol was added in the Pb-Zr-Ti compound alkoxide solution, white precipitate was generated for oxide concentration as for 0.5 weight %.

[0054] Even if it does not add excessive organic substances, such as a polydent compound, according to the production method concerning this invention, homogeneous transparent sol whose metal oxide concentration is 10 weight % or more is obtained so that clearly from the above-mentioned result. On the other hand, although it becomes possible by the conventional method to prepare stable sol partially by adding a polydent compound, compared with the sol obtained by the method concerning this invention, that metal oxide concentration is quite low.

[0055] in addition -- the above-mentioned work example -- In2O3-SnO -- although only the preparation methods of an oxide and a part of perovskite system multiple oxide sol were shown 2 system, it cannot be overemphasized that the production method concerning this invention can apply metal alkoxide to preparation of the metal oxide sol which carries out a starting material broadly.

[0056] [Form grant nature] Next, according to the method concerning this invention, it is possible to obtain various-shaped metal oxide precursor sol.

[0057] making the amount of addition of water or more into one on the preparation conditions of the sol explained in the above-mentioned work example 6 -- 2OIn3 transparent gel (work example 53) -- moreover, the transparent ITO gel (work example 54) was obtained by making the amount of addition of water or more into one on the preparation conditions of the sol explained in the above-mentioned work example 23. Moreover, by BaTiO3 and Pb(Zr, Ti) O3 system, the homogeneous gel was obtained by making the amount of addition of water or more into two.

[0058] Moreover, by removing a solvent from the sol obtained in the work example 6 under a reduced pressure, hyperviscous sol was obtained and 2OIn3 fiber was able to be manufactured by carrying out spinning of the sol of this hyperviscosity (work example 55). By the same method, manufacture of ITO, BaTiO3, and Pb(Zr, Ti) O3 fiber is also possible.

[0059] [Pellicle-izing and physical properties of thin film] Membranes were formed on the silica substrate by diluting In2O3 sol and ITO sol which were obtained in each above-mentioned work example so that oxide concentration may become 5 weight %, respectively, and carrying out the spin coat of the diluted sol at the number of rotations of 1,000rpm. thereby -- an exterior -- the homogeneous gel film was obtained. After heat-treating the obtained gel film, it evaluated by measuring the thickness and the resistance of 2OIn3 film and an ITO film. Thickness was measured using the level difference meter. Resistance was calculated as sheet resistance by 4 terminal method. The sol obtained by the comparative example 3 and comparative example 7 which were described above for comparison was formed by the same method. The characteristics of the obtained film are collectively shown in Table 6.

[0060]

[Table 6]

使用ゾル	焼成温度	膜厚（nm）	シート抵抗（Ω/□）	比抵抗（Ωcm）
実施例 6	450	80	1.50E+06	1.20E+01
6	500	75	3.50E+04	2.63E-01
17	400	70	3.60E+03	2.52E-02
18	400	75	3.20E+03	2.40E-02
19	400	75	3.60E+03	2.70E-02
20	400	80	3.10E+03	2.48E-02
21	400	85	2.50E+03	2.13E-02
21	500	80	7.40E+02	5.92E-03
22	400	85	2.70E+03	2.30E-02
23	400	85	4.80E+04	4.08E-01
24	400	80	4.10E+03	3.28E-02
25	400	80	2.30E+03	1.84E-02
26	400	75	2.80E+03	2.10E-02
27	400	75	2.90E+03	2.18E-02
28	400	90	2.70E+03	2.43E-02
29	400	65	4.10E+03	2.67E-02
30	400	90	2.60E+03	2.34E-02
比較例 3	500	35	8.50E+04	2.98E-01
7	500	40	8.30E+03	3.32E-02

[0061] 2OIn3 film and ITO film which were manufactured by the method concerning this invention are in the tendency for thickness to be thick as compared with the thing of a comparative example, and for sheet resistance to be small, and for a specific resistance value to also become low. Since the amount of remains organicity is small on the film by the method of this requiring for this invention, it is considered to be the result in which defects, such as a pore of an intramembranous part, decreased.

[0061] Moreover, the ITO sol obtained in the above-mentioned work example 21 was diluted so that oxide concentration might become 5 weight %, the diluted sol was formed with the dip coat, and the same evaluation as the above was performed. By calcinating the obtained gel film at 400 degrees C, the ITO film of 85nm of thickness, and 2.6x103ohms of sheet resistance / ** was obtained. Moreover, although the ITO sol obtained in the work example 21 was diluted so that oxide concentration might become 1 weight %, and the diluted sol was formed with the flow coat on the glass plate of a 50mm angle, the homogeneous ITO film [be / no problem] was obtained.

[0062] Next, membranes were formed on Pyrex glass by diluting the perovskite type oxide precursor sol obtained in each above-mentioned work example so that oxide concentration may become 5 weight %, respectively, and carrying out the spin coat of the diluted sol at the number of rotations of 1,000rpm. thereby -- an exterior -- the homogeneous gel film was obtained. The sol obtained by the comparative example 8 and comparative example 9 which were described above for comparison was formed by the same method. After heat-treating the obtained gel film, thickness in a membranous crystallization action

and crystallization temperature was evaluated. The characteristics of the obtained film are collectively shown in Table 7.

[0063]

[Table 7]

使用ゾル	結晶化温度 (℃)	膜厚 (nm)
実施例 34	500	80
36	500	75
40	500	80
41	450	85
42	300	80
45	400	80
46	400	80
49	450	85
50	500	80
51	450	80
52	450	80
53	400	85
比較例 9	500	15
10	500	15

[0064] As for the pellicle obtained using the sol manufactured by the method concerning this invention, the thickness at the time of crystallization is thick about 4 times compared with the thing of a comparative example. The thickness of the film formed of one spreading operation since oxide concentration cannot be made high in order to prepare stable sol is thin, and in order to obtain the thickness of the grade made into the purpose, multilayer coating is required of the method of a comparative example. Moreover, as for the pellicle by the method concerning this invention, crystallization temperature is also as low as 400 to 500 degrees C by PZT with 300 to 500 degrees C by the preparation method of sol BaTiO3 again.

[0065] As mentioned above, according to the method concerning this invention, it becomes possible to prepare precursor sol of high oxide concentration, and the application to the metal oxide Plastic solid of various form is attained. In pellicle formation, thick coating membrane is easily obtained in particular compared with the conventional method. Moreover, since there are few amounts of remains organic substances in a gel, crystallization temperature also falls.

[0066] It cannot be overemphasized that this invention can be applied to the above-mentioned precursor sol of not only a work example but various metal oxides and manufacture of a Plastic solid.

[0067]

[Effect of the Invention] According to the production method of invention concerning Claim 1, high concentration for which homogeneous membrane formation is possible at high concentration, and the metal oxide precursor sol which is homogeneous and has quantity of an organic substance which remains in the gel film after membrane formation are obtained. And the obtained precursor sol can be

fabricated in various form, especially, it will be the best for formation of the pellicle of a metal oxide, and a quality metal oxide thin film will be obtained from this precursor sol.

[0068] Moreover, it is since according to the production method of invention concerning Claim 7 there is little quantity of the organic substance which remains in a gel when metal oxide precursor sol is gelled, There is no necessity of heat-treating the metal oxide gel in high temperature for organic substance removal, for this reason, treatment at low temperature is comparatively possible, and a homogeneous metal oxide thin film without air bubbles can be formed. Moreover, the acquired metal oxide Plastic solid does not need energy excessive for eburnation, such as pellicle. Especially the method of this invention is the best for formation of the pellicle of a metal oxide, and can obtain a quality metal oxide thin film.

[Translation done.]